1937

The precipitation of ammonium molybdates by nitric acid

Alfred Eastman Newton
University of Massachusetts Amherst

THE PRECIPITATION OF AMMONIUM MOLYBDATES BY NITRIC ACID

NEWTON - 1937

DATE DUE			

THE PRECIPITATION OF AMMONIUM MOLYBDATES BY NITRIC ACID

Alfred Eastman Newton

Thesis submitted for
the degree of
Master of Science

Massachusetts State College
June 1937

TABLE OF CONTENTS

TABLE OF CONTENTS (con't)

I. INTRODUCTION

Ammonium molybdate, in nitric acid solution, has long been used as the precipitating agent in the determination of phosphorus in such substances as steels, fertilizers, soils, and biological materials. Svanberg and Struve (1) in 1847 first observed that ammonium molybdate produced a yellow precipitate in the presence of phosphoric acid. They did not, however, recognize that phosphoric acid was an essential constituent of the precipitate, to which they assigned the formula, $(NH_4)_20.5MoO_3.H_2O$. It was Sonnenschein (2), in 1851, who first proved that phosphoric acid was a normal constituent, and he utilized the precipitate for the separation of phosphorus and its subsequent determination as magnesium ammonium phosphate. Since that time many methods have been produced for the determination of phosphorus as the phosphomolybdate.

II. REVIEW OF LITERATURE

A. Methods for the Determination of Phosphorus as Phosphomolybdate.

1. Gravimetric Methods. Eggerts (3) first suggested weighing the phosphomolybdate, as a means of determining phosphorus, about 1860. Many investigators have worked over the method since, but with only minor modifications in most cases. The method is essentially as follows: The phosphomolybdate is precipitated by adding a nitric acid solution of ammonium molybdate to the neutral or faintly acid phosphate solution. It is filtered off and washed with water, 1 - 2% nitric acid, or ammonium nitrate, then dried and weighed. The individual methods may be split into two groups depending upon the temperature at which the precipitate is dried and the composition of the resulting substance. In one case the precipitate is dried between 95 - 300°C. and the residue contains ammonia, molybdic oxide, and phosphate. In the other case the precipitate is ignited just below red heat, driving out the ammonia and leaving only phosphoric anhydride and molybdic oxide.

2. Alkalimetric Method. Pemberton (4 & 5), in 1893, proposed a volumetric method for the determination of phosphorus as phosphomolybdate, depending on the acidic nature of the precipitate. The method consists essentially of decomposing the phosphomolybdate by an excess of standard alkali and titrating the excess with standard acid, using phenolphthalein as indicator.

Because of the unreliableness of the phenolphthalein end-point in the presence of ammonium salts, Neumann (6) proposed, in 1903, to remove the ammonia by boiling the solution of the precipitate in excess alkali.

When using phenolphthalein as indicator carbon dioxide present in the solution would be converted to bicarbonate at the end-point, thus using too much alkali. Because of this fact Gregersen (7), in 1907, suggested boiling the solution of the precipitate with excess acid to remove carbon dioxide; this naturally has to be done after boiling with excess alkali which removes the ammonia. The method, with many minor modifications proposed by different authors, is much used today.

3. Reduction Method. Emmerton (8), in 1888, proposed a volumetric method for the determination of phosphorus as phosphomolybdate, in Blair's "Chemical Analysis of Iron", which depends on the reduction and reoxidation of the molybdenum in the precipitate. In his original method he dissolved the phosphomolybdate in dilute ammonia, acidified the solution with sulfuric acid, and reduced the molybdenum by adding zinc to the acid solution. The reduced molybdenum was then reoxidized by standard permanganate. According to Emmerton the molybdenum was reduced by zinc and sulfuric acid to a valence condition corresponding to the formula $Mo_{12}O_{19}$.

Jones (9), in 1890, showed that nitrates must be absent from the solution while reduction is being effected, and, therefore, introduced ammonium sulfate to replace ammonium nitrate as the wash solution for the phosphomolybdate precipitate. He also suggested the use of a reduction apparatus previously described by him (10), commonly known as the "Jones reductor".

The analyses for phosphorus or of molybdenum compounds by the methods of Emmerton and Jones never showed a stochiometric ratio between molybdenum and oxygen in the reduced form of the molybdate. Both Emmerton and Jones used $Mo_{12}O_{19}$ as representing the reduced molybdate. Blair and Whitfield (11) reported $Mo_{24}O_{37}$, and Miller and Frank (12) were able to obtain reduction to a point about midway between the conditions represented by $Mo_{24}O_{37}$ and Mo_2O_5. W. A. Noyes and Frohman (13) succeeded in reducing the molybdate to Mo_2O_5 by taking pains to keep it out of contact with air, indicating that the difficulty was not due to incomplete reduction of the molybdenum, but to reoxidation by air. With a view of eliminating the difficulty Randall (14) investigated the possibility of charging the receiving flask of the Jones reductor with an oxidizer unaffected by air, which would oxidize the molybdenum thus preventing oxidation by air. He finally used a solution of ferric alum, containing phosphoric acid to decolorize it. The method, with the modifications noted, is used at the present time.

B. Composition of Ammonium Phosphomolybdate.

1. Importance of Composition in Analytical Use.

When used as a means of separating phosphorus from other substances in solution the phosphomolybdate precipitate is very useful. In such a case the composition of the substance precipitated is of little importance, the important point being only that the phosphorus be completely precipitated. On the other hand, when used as a means of

determining phosphorus, as in the general methods previously mentioned, not only must the phosphomolybdate precipitate all the phosphorus, but also the phosphomolybdate must be of a known composition which is reproducible under a known set of conditions.

2. Triammonium Phosphomolybdate. Hundeshagen (15), in 1889, showed that ammonium phosphomolybdate corresponds to the formula $(NH_4)_3PO_4.12MoO_3$ after drying at 130-150°C. regardless of the conditions of precipitation, as long as free molybdic acid is avoided. When precipitated from excess acid, washed, and dried in a desiccator over calcium chloride, the compound contains two molecules of acid and one of water, corresponding to the formula $(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$. The nitric acid, he states, is not removed by washing but is easily removed by drying at 130°C. as is the water of crystallization. From studies of the formation of this compound by the addition of nitric acid to a solution containing ammonium molybdate and ammonium phosphate, Hundeshagen concluded that the compound was formed by the condensation of two molecules of monammonium hexamolybdate $(NH_4HO).6MoO_3$, with one molecule of dihydrogen phosphate, $NH_4H_2PO_4$.

3. Diammonium Phosphomolybdate. Baxter (16), in 1905, found in a series of analyses of the phosphomolybdate that it contained only four molecules of ammonia for one of phosphoric anhydride, from which he concluded that the phosphomolybdate is the diammonium salt $(NH_4)_2HPO_4.12\ MoO_3$ instead of the triammonium salt as reported by Hundeshagen. Baxter's actual figures for the ratio $NH_3 : P_2O_5$ vary between 4.29 and 3.99. He explained the quantity of ammonia found in excess of the ratio 4.00 : 1.00 as due to

ammonium molybdate occluded with the phosphomolybdate.

4. A Mixture of Di- and Triammonium Phosphomolybdates. Posternak (17), in 1920, showed that ammonium phosphomolybdate, precipitated in the absence of ammonium salts, consists of a variable mixture of di- and triammonium phosphomolybdates, which contains phosphorus and molybdic oxide in a constant ratio, i.e., 1 : 12.

5. Summary of Composition. From the work of Hundeshagen, Baxter, and Posternak it appears that the phosphomolybdate is either $(NH_4)_2HPO_4.12\ MoO_3$ or $(NH_4)_3PO_4.12\ MoO_3$ or a variable mixture of the two; from which the ratio $NH_3 : P_2O_5$ may be variable, but the ratio $MoO_3 : P_2O_5$ should be constant, i.e., 12 : 1.

C. Composition or Contamination as Causes of Error in Phosphomolybdate Methods.

1. From Phosphoric Acid, Phosphomolybdate Ratio. A considerable amount of investigation concerning the composition of the phosphomolybdate, especially its phosphoric acid content, has been carried out in connection with the development of the gravimetric method. Data of several investigators showing the percent phosphoric acid in the phosphomolybdate after drying at various temperatures, are collected in Table I.

It is to be noted that variation in drying temperature between 95° and 300°C. has little effect on the P_2O_5 content of the precipitate. Neglecting the figure reported by Rammelsberg, which is either in error, or his precipitate was formed under unusual, undescribed, conditions, the percent P_2O_5 in the phosphomolybdate, dried at temperatures between 95° and 300°C. ranges between 3.72 and 3.77%, while that

required by the formula $(NH_4)_3PO_4.12MoO_3$ is 3.78%; and, within this temperature range, the variations in percent P_2O_5 are independent of the temperature. Apparently then, the variations in P_2O_5 content must be due to experimental error, to variable composition of the phosphomolybdate, or to contamination of the phosphomolybdate by other substances present in the solution at the time of precipitation.

Ignition of the phosphomolybdate leaves a residue of more nearly constant composition than the original precipitate, as is shown by the fact that three investigators found variation in P_2O_5 content, under these conditions, between the narrow limits 3.945 -3.96%.

Since ignition leads to more constant P_2O_5 content than does drying of the precipitate, the writer suggests that the cause of variations in P_2O_5 content may be contamination by ammonium nitrate or some other substance volatile below the drying temperature employed. Such a contaminant would not be removed by mild drying, but would be removed by ignition. However, there is some variation in P_2O_5 content even in the ignited precipitate, as the data in Table Ib show. Baxter (18) (see also 16) dried the phosphomolybdate at 290 - 300°C. for the purpose of removing ammonium nitrate, and still found slight variations in P_2O_5 content which he attributed to occluded ammonium molybdate and molybdic acid, chiefly the latter.

It is to be noted also that the P_2O_5 content of the dried precipitate approaches more nearly that required by the formula of Hundeshagen, $(NH_4)_3PO_4.12MoO_3$, than that required by the formula of Baxter, $(NH_4)_2HPO_4.12MoO_3$.

Table I-a

Per Cent Phosphoric Acid in the Phosphomolybdate

Dried Between 95°C. and 300°C.

Investigator	Drying Temperature	Per cent P_2O_5
Eggerts (3), 1860,	95° C.	3.74
Rammelsberg, (29), 1877,	100	3.90
Wood, (30), 1885,	100	3.73
Stutzer, (36), 1920,	100	3.513+
Gladdings, (31), 1896,	105	3.76
Tamm, (32), 1884,	120	3.75
Hundeshagen, (15), 1889,	150	3.72-3.77
Baxter, (18), 1902,	290 - 300	3.742
Theoretical -$(NH_4)_3PO_4.12MoO_3$(Hundeshagen)		3.783
" -$(NH_4)_2HPO_4.12MoO_3$ (Baxter)		3.818

+ Precipitated in the presence of sulfate.

Table I-b

Per Cent Phosphoric Acid in the Phosphomolybdate

Dried Between 400°C. and 500°C.

Investigator	Drying Temperature	Per cent P_2O_5
Meineke, (33), 1896,	400-500°C.	3.945
Woy, (34), 1895	400-500	3.95
Auld, (35), 1912,	400-500	3.96
Theoretical - $P_2O_5.24MoO_3$.		3.947

One may conclude then, from the data presented in Table I-a and I-b, that the phosphomolybdate is $(NH_4)_3PO_4.12MoO_3$, at least after drying, and that the variations in P_2O_5 content of the precipitate are due to contamination by ammonium nitrate, ammonium molybdate, and molybdic acid.

2. From Phosphoric Acid, Sodium Hydroxide Ratio. In the course of the development of the alkalimetric method for the determination of phosphorus, the molecular ratio P_2O_5 : NaOH has been determined by many investigators. This ratio is, in a way, a measure of the composition of the phosphomolybdate, at least to the extent that constant composition requires a constant value for the ratio, upon which fact the method is based. For example, if the phosphomolybdate is of the composition represented by the formula $(NH_4)_3PO_4.12MoO_3$, decomposition by alkali, using phenolphthalein as indicator, should be according to the following equation:

$$2(NH_4)_3PO_4.12MoO_3 + 46NaOH = 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H_2O$$

and the molecular ratio P_2O_5 : NaOH should be 1 : 46. If the ammonia is removed by boiling with excess alkali, as suggested by Neumann, the ratio should be 1 : 52. If the phosphomolybdate is $(NH_4)_3PO_4.12MoO_3.2HNO_3$ the ratio should be 1 : 50 without removing ammonia and 1 : 56 if the ammonia is removed. If the composition of the phosphomolybdate corresponds to the formula given by Baxter $(NH_4)_2HPO_4.12MoO_3$ the ratio should be 1 : 48 or 1 : 52. Table II shows the ratio as actually determined by several investigators together with the values required by the different formulae proposed for the phosphomolybdate.

Table II

The Molecular Ratio of Phosphoric Acid to Alkali as Determined for the Alkalimetric Method for Phosphorus.

Investigator	Molecular ratio P_2O_5 : NaOH Theoretical	Actual
A. (NH_3 not removed)		
Pemberton (4 & 5), 1893		1. : 46
Dienes (37), 1919,		1. : 46.4
Bhattacharyya (38), 1913,		1. : 48
Samson (39), 1925,		1. : 52
Theoretical $(NH_4)_3PO_4.12\ MoO_3$ (Hundeshagen)	1. : 46	
" $(NH)_4)_2HPO_4.12MoO_3$ (Baxter)	1. : 48.	
" $(NH_4)_3PO_4.12MoO_3.2HNO_3$, (Hundeshagen)	1. : 50.	
B. (NH_3 removed by boiling with excess alkali)		
Richards & Godden (25), 1924,		1:: 52
Iversen (40), 1920,		1 : 54.2 - 1 : 57.2
Heubner (41), 1920,		1 : 54.4
Jodidi, (42), 1915,		1 : 54.4
Neumann (6), 1903,		(1 : 56
Gregersen (7), 1907,	assumed	(1 : 56
Theoretical $(NH_4)_3PO_4.12MoO_3$	1 : 52	
" $(NH_4)_2HPO_4.12MoO_3$	1 : 52	
" $(NH_4)_3PO_4.12MoO_3.2HNO_3$	1 : 56	

A glance at Table II shows that the molecular ratio P_2O_5 : NaOH is not constant, and, in many cases, does not correspond to the ratio required by any of the formulae proposed to represent the phosphomolybdate. In view of the statement made by Posternak, that the phosphomolybdate is a variable mixture of di- and triammonium phosphomolybdate, one would not expect the ratio to be constant, if the ammonia is not removed by boiling with excess alkali before neutralization, because the required ratios for the di- and triammonium compounds are not the same under these conditions. However, if the ammonia is removed, the required ratio is the same for both, and under these conditions one would expect to obtain a constant value experimentally for the ratio, i.e., 1. : 52 if the phosphomolybdate is $(NH_4)_3PO_4.12MoO_3$ or $(NH_4)_2HPO_4.12MoO_3$, and 1. : 56 if it is $(NH_4)_3PO_4.12MoO_3.2HNO_3$ or $(NH_4)_2HPO_4.12MoO_3.2HNO_3$. Richards and Godden (25) actually obtained the ratio 1 : 52, which indicates that under certain conditions the composition is either $(NH_4)_3H$- or $(NH_4)_3$-$PO_4.12MoO_3$, or a mixture of the two, and the $-2HNO_3$ postulated by Hundeshagen is absent. For the most part, however, the ratios obtained are higher than 1 : 52, indicating either that part or all of the HNO_3 postulated by Hundeshagen is present, or that the phosphomolybdate is contaminated by some acidic substance or some ammonium salt. If the variation in ratio is due to HNO_3 alone, the ratio should never be higher than 1 : 56. Actually it is higher in one case cited in Table II. While this does not exclude the possibility of a variable amount of nitric acid being contained in the phosphomolybdate, it does indicate that some other

contaminant must be taken into account also. The only possible acidic substance which could be present is MoO_3 in excess of that required by the formulae cited; possible ammonium salts are ammonium molybdate, nitrate and sulfate. Kilgore (19) has indicated that molybdic acid and ammonium molybdate are contaminants. Kleinmann (20) has suggested occlusion of ammonium nitrate by the phosphomolybdate as an explanation of variable results obtained by him using the alkalimetric method. Falk (21) has shown the presence of sulfate in the phosphomolybdate precipitated from a solution containing sulfate and he has suggested that this "phosphosulfomolybdate" may be variable in composition thus causing variations in the molecular ratio, P_2O_5 : NaOH as noted in Table II.

Apparently then, the composition of the phosphomolybdate is more or less definite, being either di- or triammonium phosphomolybdate or a mixture of the two; and the difficulties encountered in the use of the phosphomolybdate as a means of determining phosphorus are due to contamination of the phosphomolybdate by excess molybdate and ammonium salts. If this is the true state of affairs, contamination must be caused by more or less specific conditions and substances.

It would be interesting to tabulate the percents of P_2O_5 with the amounts of ammonium ion present, if this data were available, to see if there were any correlation between the concentration of ammonium ion in solution and the per cent ammonia in the precipitate; such correlation might be expected from consideration of the mass action law if the precipitate is a mixture of di- and triammonium salts.

D. Causes of Contamination of the Phosphomolybdate.

A great deal of investigation has been carried out concerning the cause of contamination of the phosphomolybdate, and the effect of certain substances on the precipitate. Ammonium sulfate, ammonium nitrate, and free acid are the most important for these are present in most cases during formation of the phosphomolybdate.

1. Effect of Sulfate. Carpenter (22) and Hibbard (23) in studying the alkalimetric method found that the presence of sulfates at the time of precipitation led to high results, which, Hibbard stated, was due to precipitation of excess molybdate, the excess molybdate naturally using excess alkali in neutralization.

Falk (21) showed that the phosphomolybdate, when precipitated in the presence of sulfate, contained sulfate as well as an excess of molybdic oxide.

Posternak (17) found that the phosphomolybdate precipitated in the presence of 5 per cent or more of ammonium sulfate is a complex mixture of the type $8(NH_4)_3(MoO_3)_{12}PO_4+(NH_4)_2(MoO_3)_8SO_4$, in qualitative agreement, at least, with Falk's findings that the phosphomolybdate precipitated under these conditions contains sulfate as well as excess MoO_3.

2. Effect of Nitrate. Ammonium nitrate affects the phosphomolybdate in much the same way as does ammonium sulfate, but to a lesser extent. According to Hehner (24), Kilgore (19), Baxter (16) and Hibbard (23) separation of excess molybdic acid is promoted by ammonium nitrate.

Posternak (17) found that the phosphomolybdate, formed in the presence of 5 per cent or more of ammonium nitrate contained nitrate and an excess of molybdic oxide. He described the composition of the substance precipitated as a complex mixture of the type $16(NH_4)_3(MoO_3)_{12}.PO_4+NH_4(MoO_3)_4NO_3$.

3. Effect of Free Acid. Ammonium phosphomolybdate is not precipitated from a neutral solution of ammonium phosphate and ammonium molybdate. Hundeshagen (15) showed that from 23 to 26 mols of nitric acid are necessary for complete precipitation of one mol of phosphate from a mixture of ammonium molybdate, ("$(NH_4)_2MoO_4$"), and diammonium phosphate ($(NH_4)_2HPO_4$). In the presence of excess "$(NH_4)_2MoO_4$" it was found necessary to add 11 mols of nitric acid for every 6 mols of excess molybdate before precipitation was complete. He also showed that up to 80 mols of nitric acid for each mol of $PO_4^{\equiv}$ could be added before the phosphomolybdate became appreciably soluble.

Hibbard (23) states that nitric acid retards the precipitation of the phosphomolybdate and of excess molybdic acid also whereby inferring, which is common knowledge, that a certain minimum concentration of acid is necessary to prevent the precipitation of excess molybdate with the phosphomolybdate which agrees with Baxter (18).

No data has been found concerning the amount of acid necessary to prevent the separation of excess molybdate or molybdic acid with the phosphomolybdate. Apparently then, ammonium nitrate, ammonium sulfate, and free acid are all causes of contamination of the phosphomolybdate, and since

these substances are necessarily present in the solution from which the phosphomolybdate is precipitated, the conditions of precipitation must be accurately controlled to prevent contamination.

4. Effect of Small Amounts of Acid on Ammonium Molybdate; no Phosphorus Present. In connection with the problem of the effect of free acid in causing contamination of the phosphomolybdate, it is of interest to note the effect of acid on ammonium molybdate itself, when no phosphorus is present.

A number of complex compounds containing ammonia and molybdenum have been prepared by several investigators by the addition of small amounts of hydrochloric acid to ammonium paramolybdate ("ordinary" ammonium molybdate). Many of these complex compounds are only slightly soluble in water, or, in acid of the concentration used in their preparation.

Klason (26) has prepared several such compounds by the addition of N-HCl to ammonium paramolybdate. Three of these are written below with the formulae as given by Klason:

diammonium trimolybdate, $(NH_4)_2O.3MoO_3.3H_2O$

ammonium tetramolybdate, $3NH_3.6MoO_3.5H_2O$

triammonium pentadecamolybdate, $3NH_3.12MoO_3.12H_2O + 3MoO_3.8H_2O$

In the same manner Mylius (27) prepared ammonium octomolybdate $(NH_4)_2O.8MoO_3.11H_2O$.

Posternak (28) in the course of an investigation of the nature of these ammonium molybdates, has prepared several of these compounds which he calls "condensed ammonium molybdates". He prepared them by adding increasing quantities of hydrochloric acid to a saturated solution of ammonium paramolybdate. He assigns to this series of compounds the general formula,

$$(NH_4O)_3MoO(OMoO_2)_mOMoO(ONH_4)_3 + nH_2O$$

where m is always greater than five and not greater than eleven. Among those prepared, which are only slightly soluble in water are the following:

hexammonium nonamolybdate, $(NH_4O)_3MoO(OMoO_2)_7OMoO(ONH_4)_3 . 7H_2O$

hexammonium undecamolybdate, $(NH_4O)_3MoO(OMoO_2)_9OMoO(ONH_4)_3 . 8H_2O$

trihydroxytriammonium tridecamolybdate, $(NH_4O)_3MoO(OMoO_2)_{11}OMoO(OH)_3 . 19H_2O$

Posternak concludes that the tridecamolybdate is the normal form of molybdate in acid media, but that the condensation is hindered by alkali, especially ammonia, thus forming hexabasic polymolybdates intermediate between paramolybdate (m = 5 in general formula above) and tridecamolybdate (m = 11). He suggests and presents some evidence to indicate, that normal ammonium molybdate "$(NH_4)_2MoO_4$" is actually an hexabasic trimolybdate $(NH_4O)_3MoO.(OMoO_2)OMoO(ONH_4)_3$ analogous to those described above.

If the phosphomolybdate is contaminated by excess molybdic acid or ammonium molybdate, it might be expected

that the contaminant would be of the nature of some of these condensed ammonium molybdates, which are only slightly soluble in water and dilute acid. And, if ammonium nitrate causes the precipitation of a nitro molybdate when phosphorus is present, it might be expected that ammonium nitrate would likewise cause the precipitation of a nitro molybdate with these condensed ammonium molybdates, when no phosphorus is present.

E. Summary of Review of the Literature. A review of the literature indicates then:

(1) That ammonium phosphomolybdate is either $(NH_4)_3.PO_4.12MoO_3$ or $(NH_4)_2HPO_4.12MoO_3$ or a variable mixture of the two.

(2) That difficulties in the use of the phosphomolybdate as a means of determining phosphorus are caused by contamination or the phosphomolybdate by molybdic oxide, ammonium molybdate, ammonium nitrate, and ammonium sulfate.

(3) That contributing causes of contamination of the phosphomolybdate by these substances are ammonium nitrate, ammonium sulfate, and free acid present at the time of precipitation of the phosphomolybdate.

(4) That the molybdate contaminant may be of the nature of condensed ammonium molybdates, in which case free acid becomes a very significant cause of contamination.

III. PURPOSE OF INVESTIGATION

The purpose of the present investigation was to determine the effects of nitric acid on ammonium molybdate when no phosphorus is present, i.e., the range of acid concentration in which precipitation of molybdate occurs, the composition of the substances precipitated, and the effect of ammonium nitrate on these factors, with a view of throwing some light on the importance of these complex molybdates as possible contaminants of ammonium phosphomolybdate, and conditions necessary to prevent such contamination.

Since Posternak and others have already described several such compounds, analyses of several of the precipitates were carried out for the purpose of comparison with those already described in the literature.

IV. EXPERIMENTAL WORK

A. General Statement of Procedure.

For the experimental work solutions of ammonium molybdate, represented by the symbol $(NH_4)_2MoO_4$, were prepared by adding ammonia to ordinary ammonium molybdate. Solutions were prepared as required, which were 2.0 molar, 1.0 molar, 0.50 molar and 0.25 molar, and standardized by determining ammonia and molybdenum in aliquot portions. The ammonia was measured by Kjeldahl distillation, the molybdenum by reduction in a Jones reductor and reoxidation by permanganate.

Solutions of ammonium molybdate, $(NH_4)_2MoO_4$, one molar and above, were unstable and consequently were standardized immediately before use.

In Part I of the experimental work portions of each standard solution of ammonium molybdate were mixed with equal volumes of standard nitric acid of different concentrations, and the time elapsed between mixing and the first indications of precipitation was noted. By varying the concentration of the acid used, the limits of the range of precipitation were determined. The process was repeated in Part II, using solutions of nitric acid of the same concentration as before, but in addition each solution of acid was two molar in ammonium nitrate. In Part I, therefore, there were prepared four series of solutions.

Part I

(1) Series I_A, 1.0M in $(NH_4)_2MoO_4$ containing varying amounts acid.
(2) Series II_A, 0.50M " " " " "
(3) Series III_A, 0.25M " " " " "
(4) Series IV_A, 0.125M " " " " "

Part II

In the second part four similar series of solutions:

(1) Series I_B, 1.0M in $(NH_4)_2MoO_4$ & NH_4NO_3 cont. varying amounts acid
(2) Series II_B, 0.50M " 1.0M" " " " "
(3) Series III_B, 0.25M " " " " " " "
(4) Series IV_B, 0.125M " " " " " " "

After standing for a period of time varying between two weeks and two months the precipitates, where such had formed, were filtered off from the solutions, washed with cold water and dried in air, in the dark, at room temperature. The precipitates were analyzed for ammonia by the Kjeldahl method, using 0.02N HCl and NaOH, and a saturated water solution of methyl red as indicator; the molybdic oxide (MoO_3) content was determined by reduction in a Jones reductor and reoxidation by 0.1N potassium permanganate. The solutions, after separation from the precipitates, were analyzed for MoO_3 by the same method.

B. Range of Precipitation

Part I. No Ammonium Nitrate Present

The results of this portion of the work are collected in Table III, which shows the ammonium molybdate concentration, the ratio of ammonium molybdate to acid, and the time elapsed between mixing of the molybdate with acid and the appearance of a precipitate. In Series I the ammonium molybdate is one molar. Precipitation occurs in these solutions when the nitric acid is between approximately 1.15 and 5.0 molar, or when the ratio HNO_3 ; MoO_3 in the solution is between 1.15 and 5.0. In the 1.15 molar solution precipitation occurs after standing about 30 days. Increasing the concentration of acid in the solution shortens the time required for precipitation. When the acid concentration reaches 1.61 molar precipitation occurs in 3 to five seconds. As the acid concentration is increased further there is little change in the time required for precipitation until the strength of the acid becomes greater than 3 molar. In such a solution precipitation occurs in 30 seconds. As the acid concentration is increased from this point the time required for precipitation also rapidly increases. In 4.02 molar solution precipitation occurs in from 12 - 15 minutes, and in 5.03 molar there is no precipitation for about two weeks, and then only a small amount gradually increasing over a long period of time.

Table III

Time Required for Precipitation to Begin after Mixing Ammonium Molybdate Solution with Nitric Acid

A. No ammonium nitrate added. B. One mol per liter ammonium nitrate added.

HNO_3 / MoO_3	Series I $(NH_4)_2MoO_4$ conc. 1.0M		Series II $(NH_4)_2MoO_4$ conc. 0.50M		Series III $(NH_4)_2MoO_4$ conc. 0.25M		Series IV $(NH_4)_2MoO_4$ conc. 0.125M	
	A	B	A	B	A	B	A	B
1.15	30 d.							
1.20	30 h.							
1.25			4 d.	2 d.				
1.30	3 h.		36-40 h.	5 h.	--			
1.40	30 m.		3 h.	25 m.	4-5 d.	7.5 h.	--	ca. 7 d.
1.50	9-10 m.		2 h.	8-9 m.	3-3.5 d.		--	ca. 7 d.
1.60	3 -5 s.							
1.70			1 m.		10-12 m.	1 m.	8.75 h.	6 m.
1.80			10-15 s.		3.5-4 m.		4.00 h.	4 m.
1.90			5 s.		2 - 4 m.			
2.00			10-15 s.		1 m.	20 s.		
2.25			15-20 s.		1 - 2 m.			
2.50					1.5-2.5 m.			
3.00	30 s.		1-1.5 m.	0.S.	2 - 3 m.	30 s.	7 h.	1 m.
4.00	12-15 m.		15 m.	20 m.	20 m.	4-5 m.	15-20 h.	2 m.
4.50			4 h.					
5.00	ca. 14 d.		ca. 21 d.	ca.14 d.	6 - 12 h.	1.7 h.	15-20 h.	5 m.
5.50					48 h.			
6.00					ca 30 d.	7 d.	2 d.	40 m.
7.00					--			
8.00								--

d. = days m. = minutes
h. = hours s. = seconds

Results, similar to those of Series I, were observed in the solutions of Series II, III and IV, in which the concentrations of ammonium molybdate were 0.50 molar, 0.25 molar and 0.125 molar respectively.

Considering acid concentration: Precipitation occurs from 0.50 molar ammonium molybdate, Series II, when the acid is between the approximate limits 0.63 and 2.52 molar, or when the ratio HNO_3 : MoO_3 is between 1.25 and 5.0.

Considering the time factor: Precipitation occurs in four days from 0.63 molar acid and the time decreases as the acid concentration increases, until the acid reaches 0.96 molar, when precipitation occurs in 5 seconds. Increasing the acid concentration up to 2.01 molar gradually lengthens the time, precipitation occurring in 15 minutes at this concentration. Further increase in acid rapidly lengthens the time, precipitation occurring from 2.26 molar acid in about three weeks.

In 0.25 molar ammonium molybdate precipitation begins when the acid is between 0.33 and 0.35 molar and continues until it is raised to between 1.51 and 1.76 molar. Rapid decrease in precipitation time occurs as the acid increases from 0.35 to 0.50 molar, or in terms of the ratio HNO_3 : MoO_3, 1.40 to 2.00, precipitation occurring in about one minute at 2.00. The time then increases gradually as the acid is made stronger until, in 1.0 molar acid, ratio 4.00, precipitation occurs in about 20 minutes; in 1.51 molar acid, ratio 6.00, precipitation

occurs in about 30 days and in 1.76 molar acid, ratio 7.00, there was no precipitate in three months.

In .125 molar ammonium molybdate solutions precipitation occurs when the acid is between .188 to .213 molar, ratio 1.5 - 1.7, and .75 to .87 molar, ratio 6 - 7. As in the stronger solutions the time required for precipitation increases as the ratio HNO_3 : MoO_3 is varied either up or down from a value of about 2.00 : 1.00.

It is evident from the data presented that the range of precipitation of molybdate by acid for various concentrations of molybdate, is nearly constant in terms of the ratio HNO_3 : MoO_3. Precipitation occurs in the shortest time when the ratio HNO_3 : MoO_3 is about 2.00 : 1.00. Such a ratio means that the solution contains just enough acid to convert ammonium molybdate $(NH_4)_2MoO_4$, to molybdic acid, H_2MoO_4, from which one might expect that the substance precipitated is molybdic acid. Actually, however, the precipitate formed is not molybdic acid, as will be shown in the discussion of the composition of these precipitates.

For any given ratio HNO_3 : MoO_3 precipitation occurs more quickly the more concentrated the molybdate, as would naturally be expected. Thus, for example, when the ratio is 1.50 precipitation occurs in 9 to 10 minutes from 1.0 molar solution, in 2 hours from .50 molar molybdate, in 3 to 3.5 days from .25 molar molybdate, and not at all (45 days) from .125 molar solution. Such a relation holds throughout the range, except near the upper limit, in which

dase precipitation seems to occur more quickly from dilute molybdate solution than from concentrated molybdate.

Part 2. Precipitation in the Presence of Ammonium Nitrate.

The range of acid concentration within which precipitation of molybdate occurs, in the presence of 1.0 mols of ammonium nitrate, as well as the time required for precipitation to begin within this range, has been shown in Table III. It may be noted that the range of precipitation is practically the same in the presence of ammonium nitrate as when ammonium nitrate is absent. Within the precipitation range the time required for precipitation to begin decreases as the acid concentration is increased until the value of the ratio HNO_3 : MoO_4 is about 2 : 1, just as in the solutions containing no added ammonium nitrate. The time required for a precipitate to form remains about constant as the acid concentration is increased further, to a value of the ratio HNO_3 : MoO_3 of about 4 : 1, and then increases rapidly as the acid concentration is increased from this point; again similar to the behavior when no ammonium nitrate is present. For example, precipitation occurs in 0.50 molar ammonium molybdate solution when the acid concentration is between the approximate limits of 0.63 molar and 2.52 molar, or when the ratio HNO_3 : MoO_3 is between 1.25 and 5.0, whether ammonium nitrate is added to the solution or not. In the presence of ammonium nitrate,

precipitation occurs in 0.63 molar nitric acid, ratio HNO_3 : MoO_3 = 1.25, in 2 days; when the ratio HNO_3 : MoO_3 reaches 1.50 precipitation occurs in 8 to 9 minutes; as the acid concentration is increased further there is little change in the time required for precipitation until the ratio HNO_3 : MoO_3 reaches 4.00; at this point, acid concentration 2.01 molar, precipitation begins in 20 minutes, but when the acid concentration is increased to 2.26 molar, ratio 5.00, there is no precipitation for two weeks.

Comparison of the A and B portions of each series listed in Table III indicates that ammonium nitrate does have a distinct effect on the length of time required for precipitation to begin. For example, when the ratio HNO_3 : MoO_3 is 1.40, precipitation occurs from 0.50 molar ammonium molybdate in 3 hours when no ammonium nitrate is present, and in 25 minutes when one mol per liter of ammonium nitrate has been added. From 0.25 molar ammonium molybdate precipitation occurs in 4.5 days when no ammonium nitrate is present, and in 7.5 hours when the solution is one molar in added ammonium nitrate. From .125 molar ammonium molybdate there is no precipitation when no ammonium nitrate is present, but when the solution is one molar in added ammonium nitrate precipitation occurs after about a week. The same general relationship holds throughout the range of precipitation. It may be stated, therefore, that the addition of ammonium nitrate decreases the time required for a precipitate to form. Reasoning from this fact it is to be supposed that ammonium nitrate would also

extend the limits of the range of precipitation to some extent, but the effect is not great enough to be shown by the results of the present work, except at the lower limit of the range of precipitation from .125 molar ammonium molybdate solutions. In this case precipitation occurred in the presence of ammonium nitrate when the acid concentration was .176 molar, but when no ammonium nitrate was added no precipitation took place at this acid concentration; it was necessary to increase the acid concentration to .213 molar before precipitation was obtained.

C. Per Cent Precipitation

1. When no Ammonium Nitrate is Added.

The per cent of the molybdate precipitated from solution by nitric acid varies in a manner very similar to that already shown for the time required for precipitation to occur. The per cent precipitation increases as the acid concentration is increased to a certain point, then remains practically constant for further addition of acid, and finally decreases as the acid concentration is still more increased. That this should be true is to be expected, because the time required for precipitation to occur and the per cent of the molybdate precipitated in a given length of time are both measures of the rapidity of the precipitation reaction. The per cent precipitation from .25 molar and .50 molar molybdate solution

reaches a maximum of about 99% when the ratio HNO_3 : MoO_3 in the solution is 1.80 and continues so as the acid concentration is increased until the ratio exceeds 2.25 or 2.50. As the acid concentration is increased further the per cent precipitation gradually decreases to about 90% when the ratio is 4.00, and then decreases rapidly to practically zero when the ratio is 6.00. The per cent precipitation from .125 molar molybdate solutions does not vary in exactly this way. In this case the per cent precipitation increases rapidly from zero, when the ratio HNO_3 : MoO_3 is 1.50, to 62.4 when the ratio is 1.80. As more acid is added the per cent increases gradually to a maximum of 86.0, when the ratio is 4.00, and then drops quickly to practically zero when the ratio is 5.00. The actual data are shown in Table IV.

2. In the Presence of Ammonium Nitrate.

The effect of ammonium nitrate is exactly as would be predicted from its effect on the time required for precipitation to begin. In each case where the precipitation is less than 99% without ammonium nitrate present, precipitation is increased by the presence of ammonium nitrate, and the increase is greater the less the amount precipitated without it. In the presence of ammonium nitrate 65.6% of the molybdate is precipitated from .125 molar solution when the ratio HNO_3 : MoO_3 is 1.40. When ammonium nitrate is not present there is no precipitation at all. When the ratio is 1.70, 31.2% is precipitated when no ammonium nitrate is added, and

Table IV

Per Cent Precipitation of Molybdate from 0.125 Molar Ammonium Molybdate Solution by Nitric Acid and Ammonium Nitrate

Ratio HNO_3 : MoO_3	Per cent Precipitation A No $(NH_4)NO_3$ added	Per cent Precipitation B 1.0 mol/liter NH_4NO_3 added
1.40	0.00	65.6
1.50	0.00	88.8
1.70	31.2	89.6
1.80	62.4	--
3.00	82.4	93.0
4.00	86.0	--
5.00	67.2	67.2
6.00	00.0+	44.4

89.6% is precipitated in the presence of ammonium nitrate. When the ratio is 3.00, 82.4% is precipitated without ammonium nitrate and 93% is precipitated in the presence of ammonium nitrate. Comparison throughout the range of precipitation may be made by reference to Table IV.

3. Summary of Degree of Precipitation

It has been shown that the presence of ammonium nitrate decreases the time required for precipitation to occur when nitric acid is mixed with ammonium molybdate, and also that ammonium nitrate increases the per cent of the molybdate precipitated. This could be due either to a decrease in the acidity of the solution, or to a common ion effect. If due to a decrease in acidity of the solution precipitation should be increased by ammonium nitrate only if the ratio HNO_3 : MoO_3 is greater than its value when maximum precipitation occurs without ammonium nitrate. That this is not the case has been already demonstrated. Precipitation is increased by ammonium nitrate throughout the range. It may be concluded, therefore, that ammonium nitrate has an ion common with one in the precipitate formed. In the discussion of the composition of these precipitates it will be shown that they do contain the ammonium ion.

D. Application to Determination of Phosphorus

It has been shown that substances containing molybdenum and presumably some ammonia are precipitated from solutions of ammonium molybdate by nitric acid, or by nitric acid and ammonium nitrate. It has been shown that precipitation occurs when the ratio of acid concentration to molybdate concentration in the solution is between the approximate limits of 1.5 : 1 and 6 : 1, and that within these limits the time elapsed between mixing of acid and molybdate is shorter when ammonium nitrate is present than when it is absent. Hundeshagen (15) has shown that between 25 and 26 mols of acid are necessary for complete precipitation of one mol of phosphorus as ammonium phosphomolybdate. For precipitation of one mol of phosphorus 12 mols of MoO_3 are necessary according to the formula for the phosphomolybdate, $(NH_4)_3PO_4.12\ MoO_3$. From which, the ratio HNO_3 : MoO_3 necessary for precipitation of one mol of phosphorus is approximately 2 : 1, which is well within the range of precipitation of molybdate without phosphorus, as found in this investigation. Apparently then, it would not be possible to precipitate the phosmphmmolybdate in the presence of a minimum amount of acid without coprecipitation of excess molybdate. Hundeshagen (15) has also shown that a maximum of 80 mols of acid per mol of phosphorus may be present without appreciable dissociation of the phosphomolybdate precipitate when the molybdate is not in excess. This quantity of acid in the presence of the 12 mols of MoO_3

necessary to precipitate 1 mol of phosphorus makes the ratio HNO_3 : MoO_3 in the solution about 6.7 : 1 which is only slightly above the range within which precipitation of molybdate without phosphorus occurs. Presumably, however, the phosphomolybdate would precipitate immediately so that the ratio HNO_3 : MoO_3 in the solution would be increased to a safe value before precipitation of excess molybdate set in. If the molybdate is added in excess of the amount required to form the phosphomolybdate, 156 mols of acid may be added per mol of excess MoO_3 before dissociation of the phosphomolybdate begins (Hündeshagen (15)). Here then, apparently is the key to the means of precipitating phosphomolybdate without danger of the coprecipitation of excess molybdate; if the molybdate is added in excess it should be possible to add enough acid to prevent precipitation of molybdate without phosphorus and yet obtain complete precipitation of the phosphomolybdate. For example, if for the precipitation of one mol of phosphate, 13 mols of molybdate are added instead of the 12 necessary, then, according to Hundeshagen it should be possible to add 156 mols of acid without appreciable interference with the precipitation of the phosphomolybdate. If instead of 156 mols only 10 to 12 mols of acid are added there should be no interference whatsoever with the precipitation of the phosphomolybdate, and yet this amount of acid should be sufficient to prevent the precipitation of excess molybdate. The writer was unable to test this hypothesis due to lack of time.

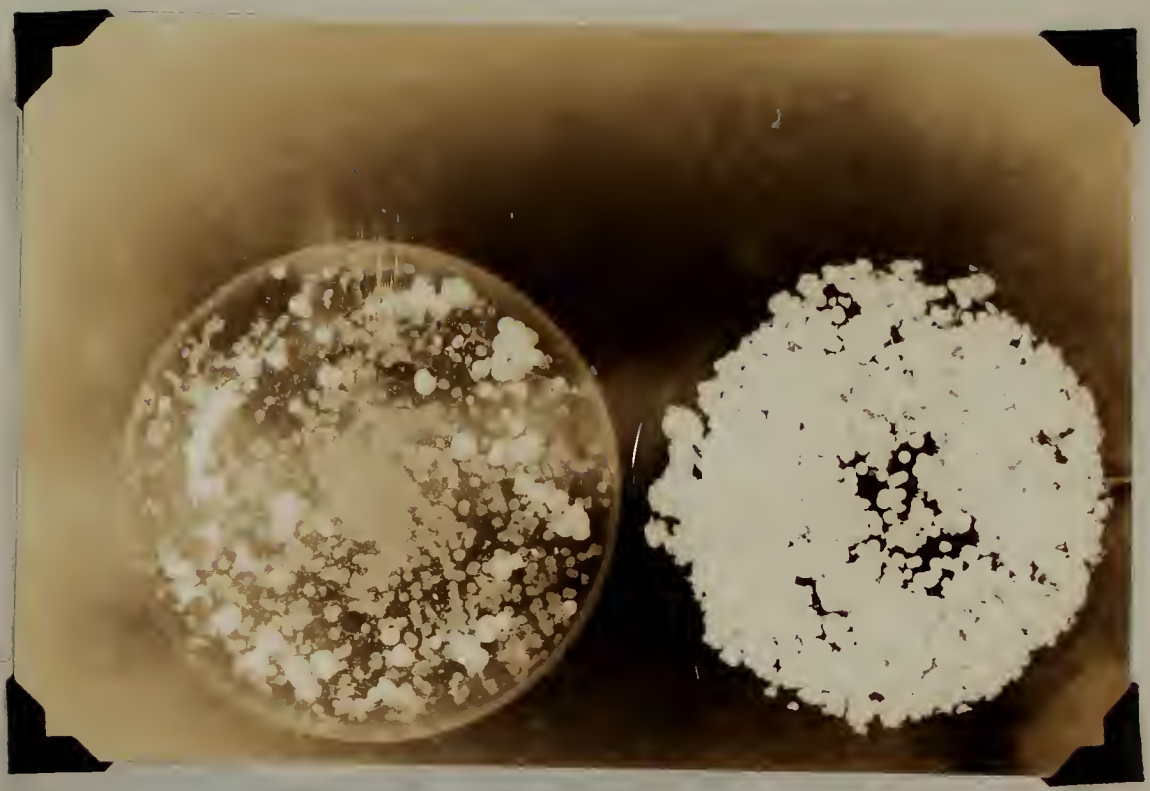
E. Manner of Crystal Growth of Substances Precipitated

As a matter of interest photographs of several of the substances precipitated, together with their composition if determined, are shown in Figures I to IV, pages 33 to 36 These photographs are views of the bottom of the flasks in which precipitation took place, so that they show the natural form of crystal growth, which is much more characteristic of a particular set of conditionsof precipitation than is the form of the individual crystal. The form of the individual crystal id dependent on the chemical composition of the substance precipitated. That there is variation in the composition of the substances studied will be shown under the discussion of composition. But apparently the slight differences in oomposition are not great enough to change the crystal form materially. On the other hand, the manner of crystal growth, as the substance precipitates, depends not so much on the chemical composition of the substance as it does on the concentration of its constituents in the solution and the resultant rate of crystallization. When precipitation occurs in less than one or two hours after mixing the molybdate with acid, a photograph of the precipitate shows little except a white mass, because precipitation has been too rapid for it to follow any particular pattern. Figure III_B and Figure II_A are examples. However, if the rate of precipitation is less rapid, the manner of crystal growth becomes characteristic of different solutions, depending chiefly on the ratio HNO_3 : MoO_3

in the solution, which fact one would expect since this determines also the rate of precipitation. Figure $I_{A\&B}$ shows two photographs of the precipitate in solution Series II_A, $\frac{HNO_3}{MoO_3} = 1.50$, Table III. Precipitation occurs in small globular white clusters, which at first look like small sodium hydroxide pellets. Observation under the microscope shows that each pellet is composed of innumerable small needles radiating from the center. Crystallization continues slowly over a long period of time, and after some time it is possible to distinguish the individual crystals with the naked eye. Figure II_B shows the early stages of a similar precipitate, Series IV_B, $\frac{HNO_3}{MoO_3} = 1.40$, Table III.

Figure IV_A is a photograph of the precipitate in the solution Series IV_A $\frac{HNO_3}{MoO_3} = 3.00$ of Table III. The formation is quite similar to that shown in Figure $I_{A\&B}$, except that the individual crystals are much larger so that they can be easily seen with the naked eye.

Figure IV_B shows the manner of growth from a solution containing less acid (Series IV_A, $\frac{HNO_3}{MoO_3} = 1.80$, of Table III). The individual crystals in $IV_{A\&B}$ are apparently identical when viewed under the microscope, but the relation between crystals in growth is distinctly different. In fact the individual crystals in all cases so far described are practically identical. Figure III_A, Series I_A, $\frac{HNO_3}{MoO_3} = 1.50$ shows the crystal form of a substance whose individual crystals are different from those already described, but similar in pattern to Figure IV_B.



A B

Figure I

Photograph of the precipitate in 0.50 molar ammonium molybdate solution when the ratio HNO_3 : MoO_3 was about 1.50.

A, represents an early stage of precipitation.

B, represents a later stage.

The composition of this substance is approximately

$$(NH_4O)_6MoO(OMoO_2)_8OMoO(ONH_4)_6.8H_2O$$

A B

Figure II

Precipitates from 0.125 molar ammonium molybdate solution in the presence of one mol per liter of ammonium nitrate.

A, when the ratio HNO_3 : MoO_3 = 1.80 (compare with Figure IV_B)

B, when the ratio HNO_3 : MoO_3 = 1.50

The composition of these precipitates was not determined.

A B

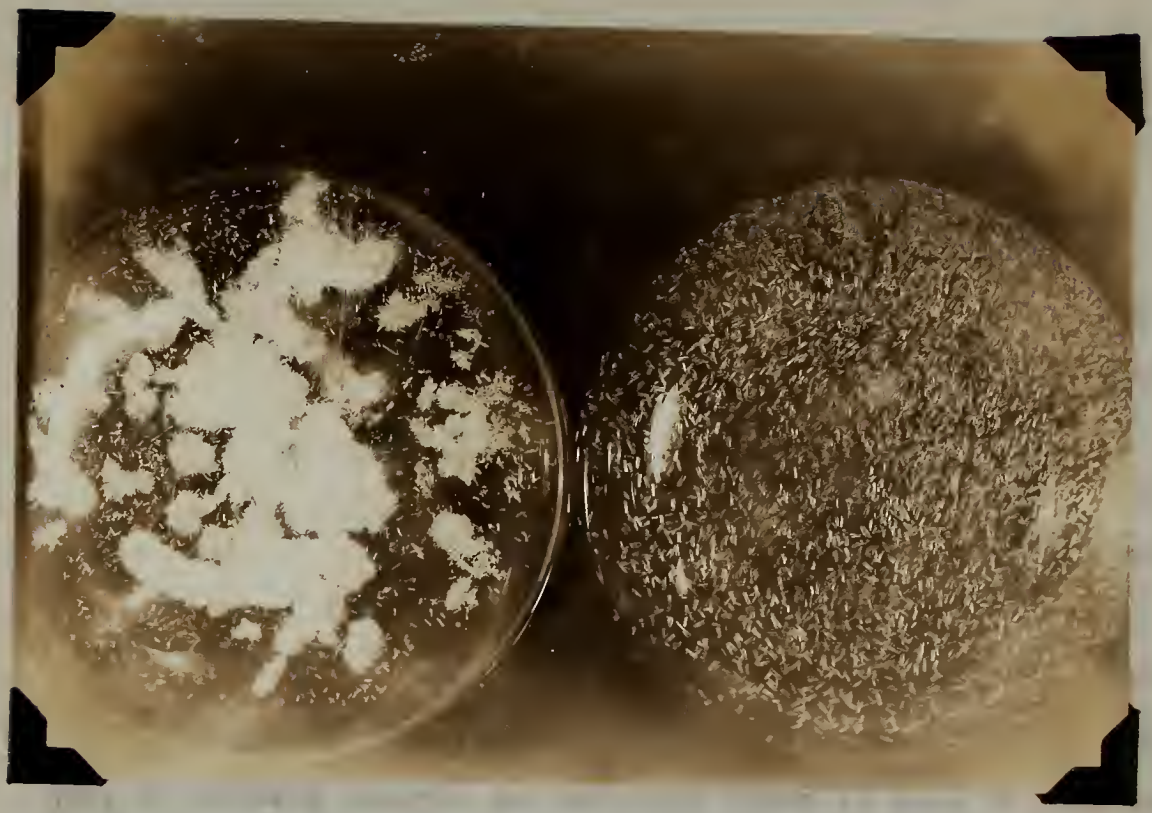
Figure III

A. Precipitate from 1.0 molar ammonium molybdate solution when the ratio HNO_3 : MoO_3 = 1.50. Composition not determined.

B. Precipitate from 0.125 molar ammonium molybdate solution, in the presence of one mol per liter of ammonium nitrate, when the ratio HNO_3 : MoO_3 = 3.00 (Compare with Figure IV_A)

Composition: approximately

$$(NH_4O)_6MoO(OMoO_2)_{11}OMoO(OH)_6.12H_2O$$



A B

Figure IV

Precipitates from 0.125 molar ammonium molybdate solution when no ammonium nitrate is added.

A, when ratio HNO_3 : MoO_3 = 3.00 (Compare Figure III_B).

Composition: Approximately equimolecular portions of

$(NH_4O)_3MoO(OMoO_2)_{11}(OMoO)(OH)_3.12H_2O$

and $(NH_4O)_2(OH)MoO(OMoO_2)_7OMoO(OH)_3.7H_2O$

B, when ratio HNO_3 : MoO_3 = 1.80 (Compare Figure II_A)

Composition: Approximately

$(NH_4O)_3MoO(OMoO_2)_{11}OMoO(OH)_3.12H_2O$

F. Composition of Substances Precipitated

1. General

It has been shown that precipitation of some substance or substances from ammonium molybdate solutions, .125 molar and stronger, occurs when the ratio HNO_3 : MoO_3 in the solution lies between 1.2 - 1.5 : 1, and 6 - 7 : 1. That these precipitates contain ammonia has been indicated from the fact that ammoniam nitrate increases the rate and amount of precipitation. That they also contain MoO_3 has been demonstrated by the fact that analysis of the solution for MoO_3, after precipitation has occurred, shows only a small percentage of the original molybdate content. Direct analysis of the precipitates shows that they do contain ammonia and molybdic oxide in more or less definite combining ratios, and in no case has it been possible to show the presence of nitrate by the colorimetric test with phenol disulfonic acid.

2. Effect of Acid Concentration.

In Table V are collected the data of a series of analyses of precipitates from 0.125, 0.25 and 0.50 molar ammonium molybdate solutions, together with the ratios MoO_3 : NH_3 calculated from the data. It may be noted that variation in the acid concentration of the solution has a marked effect on the composition of the precipitate formed. In general it may be stated that as the

acid concentration is increased the ammonia content of the precipitate decreases and the molybdic oxide content increases, or more exactly, that the ratio MoO_3 : NH_3 in the precipitate increases as the ratio HNO_3 : MoO_3 in the solution increases. For example, the ratio MoO_3 : NH_3 in the precipitate from 0.125 molar ammonium molybdate, when the ratio HNO_3 : MoO_3 in the solution is 1.70, is 4.05; when the acid concentration of the solution is increased to a ratio HNO_3 : MoO_3 of 1.80, the ratio MoO_3 : NH_3 in the precipitate is 4.33; when the ratio HNO_3 : MoO_3 in the solution is 3.00, the ratio MoO_3 : NH_3 in the precipitate is 4.38; and when the ratio HNO_3 : MoO_3 in solution is 4.00, the ratio MoO_3 : NH_3 in the precipitate is 4.50.

A similar and more marked variation in the ratio MoO_3 : NH_3 occurs in the precipitates from 0.50 molar ammonium molybdate. In this case the ratio MoO_3 : NH_3 in the precipitate increases from 1.51 when the ratio HNO_3 : MoO_3 in the solution is 1.25, to 5.33 when the ratio HNO_3 : MoO_3 in the solution is 4.00. However the ratio MoO_3 : NH_3 does not increase steadily with the acid concentration in every case. The precipitate from 0.25 molar ammonium molybdate solution, when the ratio HNO_3 : MoO_3 in the solution is 1.80, has a ratio MoO_3 : NH_3 of 3.69; when the ratio HNO_3 : MoO_3 in the solution is 1.90, the ratio MoO_3 : NH_3 in the precipitate is 4.50, when the solution ratio is 2.00, the precipitate ratio decreases to 4.40; when the solution ratio is 2.25 the precipitate ratio is again 4.50, and continues at 4.50 to 4.52 as the acid concentration of the solution is increased through a ratio HNO_3 : MoO_3 of 4.00.

Table V

Composition of Precipitates from .125M., .25M. and .50M $(NH_4)_2MoO_4$. No ammonium nitrate present.

1

0.125M $(NH_4)_2MoO_4$

Ratio $HNO_3:MoO_3$ in soln.	1.70	1.80	3.00	4.00
% NH_4 in ppt.	2.483 2.488	2.375 2.332	2.317 2.288 2.303	2.250 2.276
% MoO_3 in ppt.	85.22 85.43	85.53 85.34 85.56	85.69 85.83	85.76 85.59
Ratio $MoO_3:NH_3$	4.05	4.33	4.38	4.50

2

0.25M $(NH_4)_2MoO_4$

Ratio $HNO_3:MoO_3$ in soln.	1.80	1.90	2.00	2.25	2.50	3.00	4.00
% NH_4 in ppt.	2.760 2.782	2.254 2.244	2.298 2.306 2.295 2.303	2.243 2.247	2.250 2.261	2.263	2.249 2.238
% MoO_3 in ppt.	86.79 86.92 86.67	85.76 85.77	85.64 85.72 86.00	85.79 85.90	85.68 85.87	86.35 86.45	86.67 86.77
Ratio $MoO_3:NH_3$	3.69	4.50	4.40	4.50	4.50	4.51	4.52

3

0.50M $(NH_4)_2MoO_4$

Ratio $HNO_3:MoO_3$ in soln.	1.25	1.40	1.50	1.70	3.00	4.00
% NH_3 in ppt.	6.659 6.620	5.458 5.458	5.366 5.380	2.706 2.720	2.291 2.307	1.923 1.914
% MoO_3 in ppt.	85.47 85.36	84.26	84.69 84.69	84.05 83.64	85.56 86.21	86.76 86.68
Ratio $MoO_3:NH_3$	1.51	1.82	1.86	3.64	4.40	5.33

3. Effect of Ammonium Nitrate

The presence of ammonium nitrate in the solution from which the molybdate is precipitated in most cases increases the ammonia content of the precipitate, or in other words, decreases the ratio MoO_3 : NH_3. That the increase is not due to ammonium nitrate in the precipitate is shown by the fact that nitrate is not present. A few analyses to illustrate the point are shown in Table VI. For example, the precipitate from .125 molar ammonium molybdate solution, when the ratio HNO_3:MoO_3 is 1.80, shows a ratio MoO_3:NH_3 of 4.33 when no ammonium nitrate is added to the solution in which the precipitate formed; when one mol per liter of ammonium nitrate is added the ratio MoO_3:NH_3 in the precipitate is 4.0. When the ratio HNO_3 : MoO_3 in the solution is 3.00 the ratio MoO_3 : NH_3 in the precipitate is 4.38, without ammonium nitrate, and 4.35 in the presence of ammonium nitrate. The precipitate from 0.25 molar ammonium molybdate, when the ratio HNO_3 : MoO_3 in the solution is 2.00, shows a ratio MoO_3 : NH_3 of 4.40 when no added ammonium nitrate is present, and a ratio of 4.34 when ammonium nitrate has been added. When the ratio HNO_3 : MoO_3 is 3.00, the ratio MoO_3 : NH_3 in the precipitate is 4.34 without ammonium nitrate and 4.0 with ammonium nitrate.

Table VI

Composition of Precipitates from 0.125M and 0.25M Ammonium Molybdate Solutions.

1

0.125M $(NH_4)_2MoO_4$

	A. No NH_4NO_3 added			B. 1 mol NH_4NO_3 added		
Ratio $HNO_3:MoO_3$ in soln.	1.80	3.00	4.00	1.80	3.00	4.00
% NH_3 in ppt.	2.375 2.332	2.317 2.288 2.303	2.250 2.276	2.45 2.49	2.320 2.339	2.268 2.266
% MoO_3 in ppt.	85.53 85.34 85.56	85.69 85.83	85.76 85.59	85.49	85.80	85.96 86.25
Ratio $MoO_3:NH_3$	4.33	4.38	4.50	4.0	4.35	4.50

2

0.25M $(NH_4)_2MoO_4$

	A. No NH_4NO_3 added		B. 1 mol NH_4NO_3 added	
Ratio $HNO_3:MoO_3$ in soln.	2.00	3.00	2.00	3.00
% NH_3 in ppt.	2.298 2.295 2.306 2.303	2.263	2.326 2.324	2.46
% MoO_3 in ppt.	85.64 85.72 86.00	86.35 86.45	85.36 85.46	84.45 84.54
Ratio $MoO_3:NH_3$	4.40	4.51	4.34	4.0

That ammonium nitrate does not always increase the ammonia content of the precipitate is shown by the precipitate from .125 molar ammonium molybdate when the HNO_3 : MoO_3 ratio in the solution is 4.00. In this case the ratio MoO_3 : NH_3 in the precipitate is 4.50 whether or not ammonium nitrate has been added to the solution. This, however, appears to be the exception and not the rule.

Nitric acid and ammonium nitrate produce opposite variations in the composition of the precipitates, nitric acid decreasing the ammonia content and ammonium nitrate increasing the ammonia content. These facts indicate that the amount of ammonia in the precipitate is determined by some sort of equilibrium between ammonium ion and hydrogen ion in the solution

4. Effect of Time of Standing of Precipitate.

Another factor which influences the composition of the precipitate, in some cases, is the length of time the precipitate is allowed to stand in contact with the solution from which it formed. Two examples, precipitates from 0.25 molar ammonium molybdate solution, are shown in Table VII . The precipitate from the solution in which the ratio HNO_3 : MoO_3 was 1.80 showed a ratio MoO_3 : NH_3 of 3.69 a half hour after mixing the molybdate with the acid; after standing 43 days the ratio MoO_3 : NH_3 had increased to 4.23. The

precipitate from the solution in which the ratio HNO_3 : MoO_3 was 4.00 was found to have a ratio MoO_3 : NH_3 of 4.5 48 hours after mixing which had increased to 5.64 after 85 days.

It is to be noted that the initial precipitate contains a larger amount of ammonia than does the precipitate after standing a month or so. This fact may be due either to precipitation of a second substance containing less ammonia, or to a gradual replacement of the ammonium ion of the initial precipitate by hydrogen ion from the solution. Viewing the crystals under a microscope does not indicate a mixture of crystal forms, but, in the case of the precipitate, mentioned above, from a 0.25 molar ammonium molybdate when the ratio HNO_3 : MoO_3 in the solution is 4.00, there is a very distinct difference between the crystal form of the initial precipitate and that present after standing 85 days. The crystals of the initial precipitate are monoclinic or triclinic rods, while those of the aged precipitate are regular hexagonal prisms. From this it may be concluded that the change in composition is due to a gradual change in the composition of the original precipitate and not to the precipitation of a second substance. In addition, it has been noticed that such changes in composition occur only after initial precipitation has been rapid and only at points in the precipitation range which represent transition points between precipitates of one composition and those of another. It appears, then, that a plausible explanation of the change is

Table VII

Effect of Time of Standing on Composition of Precipitates

Precipitates from .25M $(NH_4)_2MoO_4$

Ratio $HNO_3:MoO_3$ in soln.	1.80		4.00	
Time of standing	0.5h.	43d.	48h.	85d.
% NH_3 in ppt.	2.782 2.760	2.389 2.398 2.388	2.25 2.28	1.920 1.912
% MoO_3 in ppt.	86.79 86.92 86.67	85.71 85.67 85.44	86.67 86.77	91.49 91.69
Ratio $MoO_3:NH_3$	3.69	4.23	4.5	5.64

the gradual replacement of ammonium-ion in the precipitate by hydrogen-ion from the solution, and that equilibrium between precipitate and solution is not reached over a considerable period of time. The lack of further evidence to substantiate this point makes a more definite statement impossible.

5. Simplest Formulae from Compisition.

a. Ratio $MoO_3 : NH_3 = 9 : 2$ and $9 : 6$, Diammonium and Hexammonium Nonamolybdate

As already stated, the occurrence of definite combining ratios between ammonia and molybdic oxide in the precipitates indicates that such precipitates are pure compounds. Several such ratios may be noted in Tables V, VI, and VII, but will be repeated for convenience.

Table VIII shows a series of analyses of precipitates from 0.125 molar and 0.25 molar ammonium molybdate solutions, together with the ratio $MoO_3 : NH_3$ calculated from that data.

Table VIII

Analyses of Some Precipitates from 0.125 molar and 0.25 molar $(NH_4)_2MoO_4$ Solution.

	A. No NH_4NO_3 added				B. 1 mol NH_4NO_3 added		
	1-0.125 molar $(NH_4)_2MoO_4$				2 0.25 molar $(NH_4)_2MoO_4$		
Ratio $HNO_3:MoO_3$ in soln.	A 4.00	B 4.00	A 1.90	A 2.25	A 2.50	A 3.00	A 4.00
% NH_3	2.250 2.276	2.268 2.266	2.254 2.244	2.243 2.247	2.250 2.261	2.263	2.25 2.28
% MoO_3	85.76 85.59	85.96 86.25	85.76 85.77	85.90 85.79	85.68 85.87	86.35 86.45	86.67 86.77
Ratio $MoO_3:NH_3$	4.5	4.5	4.5	4.5	4.5	4.5	4.5

The ratio MoO_3 : NH_3 in this series of precipitates is 4.5 : 1 which means that the simplest formula for the compound must contain nine molecules of molybdic oxide and two molecules of ammonia. Assuming the difference between 100% and the sum of the per cent ammonia and the per cent molybdic oxide to be water it is possible to derive the simplest formula. This formula is shown below, using the notation of Posternak (28):

$$(NH_4O)_2(OH)MoO(OMoO_2)_7OMoO(OH)_3.7H_2O$$

Theoretical %	NH_3	MoO_3
	2.252	85.83

In Table IX is shown the analysis of a single precipitate from 0.50 molar ammonium molybdate solution, from which the ratio MoO_3 : NH_3 was calculated to be approximately 1.5.

Table IX

Analysis of Precipitate from 0.50 Molar Ammonium Molybdate Solution.

Ratio HNO_3:MoO_3 in soln.	1.25
% NH_3	6.659 6.620
%MoO_3	85.47 85.36
Ratio MoO_3:NH_3	1.51

The results of this analysis correspond approximately to the composition required by the formula

$$(NH_4O)_8MoO(OMoO_2)_7OMoO(ONH_4)_8.4H_2O$$

Theoretical %	NH_3	MoO_3
	6.704	85.02

Posternak (28) has described a compound which he named hexammonium nonamolybdate and to which he assigned the formula

$$(NH_4O)_8MoO(OMoO_2)_7OMoO(ONH_4)_8.7H_2O$$

Theoretical %	NH_3	MoO_3
	6.475	82.11

This formula is identical with that calculated from the data in Table IX, except for the water content. Posternak reported $7H_2O$; the writer finds approximately $4H_2O$.

The writer was unable to find a compound reported in the literature, corresponding to the formula calculated from the data in Table VIII, but it is apparently an unsaturated salt of this same acid, nonamolybdic acid, and would be named diammonium tetrahydroxy nonamolybdate.

b. Ratio MoO_3 : NH_3 = 11 : 6 and 11 : 3, Hexammonium and Triammonium Undecamolybdate

In Table X are shown analyses from which ratios of MoO_3 to NH_3 of approximately 11 : 6 and 11 : 3 were calculated.

Table X

Analyses of Some Precipitates from 0.25 molar amd 0.50 molar $(NH_4)_2MoO_4$ Solutions.

	0.25 molar $(NH_4)_2MoO_4$	0.50 molar $(NH_4)_2MoO_4$		
Ratio $HNO_3:MoO_3$ in soln.	No. 1	No. 2	No. 3	No. 4
	1.80	1.70	1.50	1.40
% NH_3	2.782 2.760	2.706 2.720	5.366 5.380	5.458
% MoO_3	86.79 86.92 86.67	84.05 83.64	84.69 84.69	84.26
Ratio $MoO_3:NH_3$	.369 or 11:3	3.64 or 11:3	1.86 or 11:6	1.82 or 11:6

A ratio MoO_3 : NH_3 of 11 : 6 corresponds to a compound whose simplest formula contains eleven molecules of molybdic oxide and six molecules of ammonia. A ratio of 11 : 3 corresponds to eleven molecules of molybdic oxide and three molecules of ammonia. Posternak (28) has described a compound containing eleven molecules of molybdic oxide and six ammonia which he formulated as follows:

$$(NH_4O)_3MoO(OMoO_2)_9OMoO(ONH_4)_3.8H_2O$$

Theoretical %	NH_3	MoO_3
	5.414	84.08

and named hexammonium undecamolybdate. Analyses No. 3 and No. 4, Table X, correspond approximately to this composition.

If three ammonium radicals in the above formula are replaced by hydrogen ions, the formula becomes

$$(NH_4O)_3MoO(OMoO_2)_9OMoO(OH)_3.8H_2O$$

and the ratio MoO_3 : NH_3 is 11 : 3, which is the ratio calculated from the data of analyses No. 1 and No. 2, Table X. The simplest formula calculated from the data of analysis No. 1 is

$$(NH_4O)_3MoO(OMoO_2)_9OMoO(OH)_3.8H_2O$$

Theoretical %	NH_3	MoO_3
	2.782	86.42
Found (analysis No.1 Table X)	2.771	86.79

The writer was unable to find such a compound reported in the literature.

It may be noted that the per cent of ammonia and molybdic oxide recorded in analysis No. 1, Table X, is distinctly different than the per cents recorded in analysis No. 2, and yet the ratio MoO_3 : NH_3 is nearly the same for both, being about 11 : 3. This fact can be explained only as due to a difference in the water content of the two precipitates. Analysis No.1 shows about 2.77% NH_3 and 86.8% MoO_3 from which the simplest formula was calculated to be

$$(NH_4O)_3MoO(OMoO_2)_9OMoO(OH)_3.8H_2O.$$

Analysis No. 2 shows about 2.71% NH_3 and 83.8% MoO_3 from which the simplest formula was calculated to be

$$(NH_4O)_3MoO(OMoO_2)_9OMoO(OH)_3.11H_2O$$

differing from that calculated from analysis No. 1 by $3H_2O$. Whether the difference in water content was caused by some unknown variation in the manner of drying or by a difference in the conditions of formation is not evident.

c. Ratio MoO_3 : NH_3 = 13 : 3, Triammonium Tridecamolybdate.

In Table XI are shown two analyses from which the ratio MoO_3 : NH_3 was calculated to be 4.33 : 1, or 13 : 3.

Table XI

Ratio MoO_3 : NH_3 = 13 : 3

	0.125 molar $(NH_4)_2MoO_4$	0.25 molar $(NH_4)_2MoO_4$
Ratio HNO_3:MoO_3 in soln.	1.80	2.00
% NH_3	2.375 2.332	2.326 2.324
% MoO_3	85.53 85.34 85.56	85.36 85.46
Ratio MoO_3:NH_3	4.32	4.33

A ratio MoO_3 : NH_3 of 4.33 : 1.00, or 13 : 3 indicates that the simplest formula for the compound must contain 13 molecules of molybdic oxide and 3 molecules of ammonia. The simplest formula, calculated from the data in Table XI, is: $(NH_4O)_3MoO(OMoO_2)_{11}OMoO(OH)_3.12H_2O$

Theoretical %	NH_3	MoO_3
	2.325	85.36

Posternak has described a compound to which he assigned the formula $(NH_4O)_3MoO(OMoO_2)_{11}OMoO(OH)_3.19H_2O$

Theoretical %	NH_3	MoO_3
	2.199	80.72

which is identical with that calculated from the data in Table XI, except for the water content; Posternak reported $19H_2O$; the writer finds $12H_2O$.

d. Ratio $MoO_3 : NH_3 = 16 : 3$, Triammonium Hexadecamolybdate

A ratio $MoO_3 : NH_3$ of 5.33 : 1.00 or 16 :3, indicates that the simplest formula must contain 16 molecules of molybdic oxide and 3 molecules of ammonia. The precipitate from 0.50 molar ammonium molybdate solution caused by 2.01 molar nitric acid, ratio $HNO_3 : MoO = 4.00$, was found to contain 1.914 - 1.923% NH_3, and 86.68 - 86.76% MoO_3 from which the simplest formula is

$$(NH_4O)_3MoO(OMoO_2)_{14}OMoO(OH)_3.14H_2O$$

Theoretical %	NH_3	MoO_3
	1.917	86.58

The writer was unable to find such a compound described in the literature.

e. Ratio $MoO_3 : NH_3 = 17:3$, Triammonium Heptadecamolybdate.

A ratio $MoO_3 : NH_3$ of 5.67 : 1.00 or 17 : 3 means that the simplest formula of such a compound must contain 17 molecules of MoO_3 and 3 molecules of ammonia. The precipitate from .25 molar ammonium molybdate solution, when the ratio $HNO_3 : MoO_3$ in the solution was 4.00, was found to contain

1.912 - 1.920% NH_3

and 91.49 - 91.69% MoO_3

from which the simplest formula is

$$(NH_4O)_8MoO(OMoO_2)_{18}OMoO(OH)_8.6H_2O$$

Theoretical %	NH_3	MoO_3
	1.916	92.00

The writer was unable to find such a compound described in the literature.

The results are summarized in Table XII, which includes the formulae calculated, the theoretical per cents of ammonia and molybdic oxide and the per cents found. Similar formulae reported by Posternak are included for comparison.

From the discussion of the results presented in Table XII it might be supposed that all the substances analyzed in this investigation were pure compounds. However, it will be noted that several analyses are reported in Tables V, VI, and VII which do not correspond to any formula. Such ratios indicate that the substance precipitated was a mixture of two or more compounds. The fact that relatively few such precipitates were encountered indicates that the compounds described are definite compounds, for no special attempt was made to prepare pure compounds.

None of the precipitates from 1.0 molar ammonium molybdate solution were analyzed, due to lack of time. Whether or not analysis of these precipitates would produce any new material is difficult to say, but the writer is of the opinion that it would do so.

Table XII

Composition of Complex Ammonium Molybdates - Summary

	Simplest Formulae according to system of Posternak	%NH_3 Theory	%NH_3 Found	%MoO_3 Theory	%MoO_3 Found	Systematic Names
1.	$(NH_4O)_3MoO(OMoO_2)_7OMoO(ONH_4)_3.4H_2O$,	6.70	6.64	85.02	85.42	hexammonium nonamolybdate
2,	$(NH_4O)_3MoO(OMoO_2)_9OMoO(ONH_4)_3.8H_2O$,	5.41	5.41	84.08	84.55	hexammonium undecamolybdate
3.	$(NH_4O)_3MoO(OMoO_2)_9OMoO(OH)_3.8H_2O$,	2.782	2.771	86.42	86.79)	triammonium undecamolybdate
	$.11H_2O$,	2.703	2.713	84.02	83.85)	
4.	$(NH_4O)_3MoO(OMoO_2)_{11}OMoO(OH)_3.12H_2O$,	2.325	2.327	85.36	85.45	triammonium tridecamolybdate
5.	$(NH_4O)_2(OH)MoO(OMoO_2)_9OMoO(OH)_3.7H_2O$,	2.252	2.256	85.83	85.92	diammonium nonamolybdate
6.	$(NH_4O)_3MoO(OMoO_2)_{14}OMoO(OH)_3.14H_2O$,	1.917	1.919	86.58	86.72	triammonium hexadecamolybdate
7.	$(NH_4O)_3MoO(OMoO_2)_{15}OMoO(OH)_3.6H_2O$.	1.916	1.916	92.00	91.60	triammonium heptadecamolybdate
	Described by Posternak					
1.	$(NH_4O)_3MoO(OMoO_2)_7OMoO(ONH_4)_3.7H_2O$,	6.475		82.11		hexammonium nonamolybdate
2.	$(NH_4O)_3MoO(OMoO_2)_9OMoO(ONH_4)_3.8H_2O$,	5.414		84.08		hexammonium undecamolybdate
4.	$(NH_4O)_3MoO(OMoO_2)_{11}OMoO(OH)_3.19H_2O$,	2.199		80.72		triammonium tridecamolybdate

6 Theoretical Discussion.

The writer has used the notation of Posternak (28) throughout the discussion of the complex hexabasic molybdates described. Posternak has prepared and examined several such compounds, varying in degree of condensation between heptamolybdate, or para molybdate and tridecamolybdate. To this series of compounds he has assigned the type formula,

$$(NH_4O)_3MoO(OMoO_2)_mOMoO(ONH_4)_3.nH_2O$$

where m is equal to or greater than five. From the results of his investigations he concluded that tridecamolybdate, m = 11, represents the limit of condensation, and is the normal form of molybdic acid in acid medium. He stated also that acid salts are possible only at the limit of condensation. It may be noted, in Table XII, that the writer has obtained substances in which the value of m is 14 and 15, formulated according to the system of Posternak. Apparently then tridecamolybdate does not represent the limit of condensation, though it may be the normal form. It may be noted also that acid salts have been obtained in which the value of m is 7 and 9 in contradiction to Posternak's statement that acid salts are possible only when m = 11.

As noted above Posternak has assigned to these compounds the general formula,

$$(NH_4O)_3MoO(OMoO_2)_mOMoO(ONH_4)_3.nH_2O.$$

This formula indicates a chain of molybdic oxide groups with three ammonium groups attached at either end, condensation

occuring by the addition of molybdic oxide groups to the chain. The writer has found it impossible to balance, electronically, such a formula. It is possible to add molybdic oxide groups to an existing chain without upsetting the electronic balance, as in the dibasic polymolybdates,

O	O O	O O O
$NH_4OMoONH_4$	$NH_4OMoOMoONH_4$	$NH_4OMoOMoOMoONH_4$
O	O O	O O O
monomolybdate	dimolybdate	trimolybdate

but it is not possible for the resulting chain to be hexabasic unless the lowest member of the series is itself hexabasic. Electronically balanced formulae fulfilling this condition may be derived readily on the basis of a suggestion made by Werner (43) or a similar one by Copaux (44) concerning the structure of ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}.\ 4H_2O$. Werner considered the acid, $H_6Mo_7O_{24}$, of which ammonium paramolybdate is a salt, as derived from the hypothetical ortho acid, H_6MoO_6, by addition of a molybdic oxide group to each of the six oxygens; Copaux considered it as formed by the addition of an M_2O_6 group to three of the six oxygens.

In order to formulate the ortho acid electronically it is necessary that the molybdenum atom have twelve electrons around it as follows:

HO: :OH

HO: Mo :OH

HO: :OH

six belonging to the molybdenum atom and one to each hydroxyl group. This is not at all impossible electronically,

and furnishes a simple explanation of the hexabasic polymolybdates. The acid $H_6Mo_7O_{24}$ corresponding to ammonium paramolybdate, could be considered as formed by the condensation of one molecule of the ortho acid, H_6MoO_6, with six molecules of the meta acid, H_2MoO_4, or, with three molecules of the dimolybdic acid, $H_2Mo_2O_7$, with the elimination of water as follows:

$$Mo(OH)_6 + 6HO\,Mo(=O)OH \text{ ---- } Mo(O\,Mo(=O)OH)_6 + 6H_2O$$

ortho acid — meta acid — "para" acid

or

$$Mo(OH)_6 + 3HO\,Mo(=O)O\,Mo(=O)OH \text{ ---- } Mo(OH)_3(O\,Mo(=O)O\,Mo(=O)OH)_3 + 3H_2O$$

ortho acid — di acid — "para" acid

Similarly, tridecamolybdic acid could be formed by a condensation of one molecule of the "para" acid, with six molecules of the meta acid, or with three molecules of the di-acid. Acids intermediate between the "para" acid and tridecamolybdic acid could be formed by the condensation of less than six molecules of the meta acid, or less than three molecules of the di-acid with one molecule of the"para" acid. For example nonamolybdic acid could be formed as follows:

$$Mo(O\,Mo(=O)OH)_6 + 2HO\,Mo(=O)OH \text{ ---- } Mo(O\,Mo(=O)O\,Mo(=O)OH)_2(O\,Mo(=O)OH)_4 + 2H_2O$$

"para" acid — meta acid — nonamolybdic acid

or

$$Mo(O\,Mo(=O)OH)_6 + HO\,Mo(=O)O\,Mo(=O)OH \text{ --- } Mo(O\,Mo(=O)O\,Mo(=O)O\,Mo(=O)OH)(O\,Mo(=O)OH)_3 + H_2O$$

"para" acid — di-acid — nonamolybdic acid

That the unit of condensation may be the dimolybdic acid, $H_2Mo_2O_7$, is indicated by the prevalence of complexes containing an odd number of molybdenum atoms, as may be noted by reference to Table XII.

In every case one of the molybdenum atoms is different from the others in that it acts as the central atom of the complex and has twelve electrons around it, two for each of the six groups surrounding it.

Posternak concluded, from his work on complex hexabasic molybdates, that the normal salts are not dibasic but hexabasic. Thus normal ammonium molybdate, $(NH_4)_2MoO_4$ becomes $(NH_4)_6(MoO_4)_3$, or, according to the system of Posternak, $(NH_4O)_3MoO(OMoO_2)OMoO(ONH_4)_3$. In accordance with the formulae proposed above this would be:

$$\begin{array}{lcl} NH_4O & & ONH_4 \\ & & O \\ NH_4O & Mo & OMoONH_4 \\ & & O \\ NH_4O & & OMoONH_4 \\ & & O \end{array} \quad \text{or} \quad \left[\begin{array}{lcl} O & & O \\ & & \\ O & Mo & MoO_4 \\ & & \\ O & & MoO_4 \end{array}\right]^{6-} 6NH_4^+$$

Normal ammonium molybdate is an unstable compound. It is formed only in the presence of excess ammonia, and in the dry state it decomposes readily, giving off ammonia. Ammonium paramolybdate is the common form of ammonium molybdate and this salt too is formed in ammoniacal solution, but it is stable at ordinary temperature. Beyond the paramolybdate is a whole series of more condensed hexabasic polymolybdates some of which have been mentioned in this paper. The interesting point concerning these compounds is that the

degree of condensation increases with the acid concentration. If normal ammonium molybdate is a salt of the hexabasic acid, $H_6Mo_3O_{12}$, as written above, then the four OH groups linked directly to the central molybdenum atom must react as acid groups, that is, in the neutralization of the acid to form the ammonium salt the hydrogen of each OH group breaks off leaving the oxygen linked to the molybdenum. This reaction occurs only in strongly ammoniacal solution. In the formation of paramolybdic acid, $H_6Mo_7O_{24}$, from the ortho acid, H_6MoO_6, and the meta acid, H_2MoO_4, these same OH groups must behave as hydroxyl groups, the reaction being a neutralization reaction since it is accompanied by the formation of water. Ammonium paramolybdate is obtained from a solution more acid than that required for the formation of the normal salt $(NH_4)_6(Mo_3O_{12})$. The same type reaction must take place in the formation of each of the condensed acids.

As already noted the degree of condensation increases as the acid concentration of the solution increases, from which it follows that the OH groups of the acids must be changed progressively from acid groups to basic groups as the acid concentration in the solution is increased, in order to make such condensation possible; or, in other words, the presence of hydrogen ion in the solution causes the break in the group $\begin{matrix} O \\ MoOH \\ O \end{matrix}$, to occur between the $\begin{matrix} O \\ Mo \\ O \end{matrix}$ and OH rather than between the $\begin{matrix} O \\ MoO \\ O \end{matrix}$ and H and the concentration of hydrogen ion necessary to accomplish this is greater

the further the $MoO(OH)_2$ group is from the central molybdenum atom of the complex. If the condensed hexabasic molybdates described in this paper are derived from the ortho acid, H_6MoO_6, as the author has suggested, and if the mechanism of the condensation reaction is as outlined above, then these molybdates may be represented by formulae such as the following:

$$\left|\begin{matrix}\overline{MoO_4} & & \overline{MoO_4} \\ MoO_4 & Mo & Mo_2O_7 \\ \underline{MoO_4} & & \underline{Mo_2O_7}\end{matrix}\right|^{6-} \; 6NH_4^+ + 4H_2O$$

hexammonium nonamolybdate

$$\left|\begin{matrix}\overline{MoO_4} & & \overline{Mo_2O_7} \\ MoO_4 & Mo & Mo_2O_7 \\ \underline{Mo_2O_7} & & \underline{Mo_2O_7}\end{matrix}\right|^{6-} \; 6NH_4^+ + 8H_2O$$

hexammonium undecamolybdate

$$\left|\begin{matrix}\overline{MoO_4} & & \overline{MoO_4} \\ MoO_4 & Mo & Mo_2O_7 \\ \underline{MoO_4} & & \underline{Mo_2O_7}\end{matrix}\right|^{6-} \; \begin{matrix}2NH_4^+ \\ 4H^+\end{matrix} + 7H_2O$$

diammonium nonamolybdate

$$\left|\begin{matrix}\overline{MoO_4} & & \overline{Mo_2O_7} \\ MoO_4 & Mo & Mo_2O_7 \\ \underline{Mo_2O_7} & & \underline{Mo_2O_7}\end{matrix}\right|^{6-} \; \begin{matrix}3NH_4^+ \\ 3H^+\end{matrix} \; .8H_2O \text{ or } 11H_2O$$

triammonium undecamolybdate

$$\left|\begin{matrix}\overline{Mo_2O_7} & & \overline{Mo_2O_7} \\ Mo_2O_7 & Mo & Mo_2O_7 \\ \underline{Mo_2O_7} & & \underline{Mo_2O_7}\end{matrix}\right|^{6-} \; \begin{matrix}3NH_4^+ \\ 3H^+\end{matrix} + 12H_2O$$

triammonium tridecamolybdate

$$\left|\begin{matrix}\overline{Mo_2O_7} & & \overline{Mo_3O_{10}} \\ Mo_2O_7 & Mo & Mo_3O_{10} \\ \underline{Mo_2O_7} & & \underline{Mo_3O_{10}}\end{matrix}\right|^{6-} \; \begin{matrix}3NH_4^+ \\ 3H^+\end{matrix} + 14H_2O$$

triammonium hexadecamolybdate

$$\left|\begin{matrix}\overline{Mo_2O_7} & & \overline{Mo_3O_{10}} \\ Mo_2O_7 & Mo & Mo_3O_{10} \\ \underline{Mo_3O_{10}} & & \underline{Mo_3O_{10}}\end{matrix}\right|^{6-} \; \begin{matrix}3NH_4^+ \\ 3H^+\end{matrix} + 6H_2O$$

triammonium heptadecamolybdate

It is possible that the ammonia of these compounds may be present as ammonia in coordination with the central molybdenum atom of the complex, rather than as ammonium radicals as indicated above. If such is the case the formula could be written as follows:

$$\left|\begin{matrix}\overline{NH_3} & & \overline{NH_3} \\ NH_3 & Mo & NH_3 \\ \underline{NH_3} & & \underline{NH_3}\end{matrix}\right|^{6+} \begin{matrix}4HMoO_4^- \\ 2HMo_2O_7^-\end{matrix} + 4H_2O$$

hexammonium nonamolybdate

$$\left|\begin{matrix}\overline{NH_3} & & \overline{NH_3} \\ NH_3 & Mo & NH_3 \\ \underline{NH_3} & & \underline{NH_3}\end{matrix}\right|^{6+} \begin{matrix}2HMoO_4^- \\ 4HMo_2O_7^-\end{matrix} + 8H_2O$$

hexammonium undecamolybdate

$$\left|\begin{matrix}\overline{NH_3} & & \overline{H_2O} \\ NH_3 & Mo & H_2O \\ \underline{H_2O} & & \underline{H_2O}\end{matrix}\right|^{6+} \begin{matrix}4HMoO_4^- \\ 2HMo_2O_7^-\end{matrix} + 3H_2O$$

diammonium nonamolybdate

$$\left|\begin{matrix}\overline{NH_3} & & \overline{H_2O} \\ NH_3 & Mo & H_2O \\ \underline{NH_3} & & \underline{H_2O}\end{matrix}\right|^{6+} \begin{matrix}2HMoO_4^- \\ 4HMo_2O_7^-\end{matrix} + 5H_2O \text{ or } 8\ H_2O$$

triammonium undecamolybdate

$$\left|\begin{matrix}\overline{NH_3} & & \overline{H_2O} \\ NH_3 & Mo & H_2O \\ \underline{NH_3} & & \underline{H_2O}\end{matrix}\right|^{6+} 6HMo_2O_7^- + 9H_2O$$

triammonium tridecamolybdate

$$\left|\begin{matrix}\overline{NH_3} & & \overline{H_2O} \\ NH_3 & Mo & H_2O \\ \underline{NH_3} & & \underline{H_2O}\end{matrix}\right|^{6+} \begin{matrix}3HMo_2O_7^- \\ 3HMo_3O_{10}^-\end{matrix} + 11H_2O$$

triammonium hexadecamolybdate

$$\left|\begin{matrix}\overline{NH_3} & & \overline{H_2O} \\ NH_3 & Mo & H_2O \\ \underline{NH_3} & & \underline{H_2O}\end{matrix}\right|^{6+} \begin{matrix}2HMo_2O_7^- \\ 4HMo_3O_{10}^-\end{matrix} + 3H_2O$$

triammonium heptadecamolybdate

The evidence necessary to determine which, if either, of these type formulae are correct, is not at hand. But it should be possible to indicate whether the ammonia is part of the negative or the positive portion of the complex, and whether or not any of the molybdenum is associated with the positive portion, by determining the direction of migration of the ammonia and molybdenum in solution under the influence of an electric field.

V. SUMMARY

1. Nitric acid causes precipitation of molybdate from $(NH_4)_2MoO_4$ solutions when the ratio HNO_3 : MoO_3 is between the approximate limits 1.25 : 1 and 7 : 1.

2. The time required for a precipitate to form increases as the acid molybdate ratio is varied in either direction from a value of about 2 : 1.

3. The time required for a precipitate to form increases as the molybdate concentration is decreased.

4. The per cent of the molybdate precipitated decreases as the ratio HNO_3 : MoO_3 is varied in either direction from a value of about 2 : 1.

5. Ammonium nitrate decreases the time required for a precipitate to form, and increases the per cent of the molybdate precipitated.

6. The precipitates contain ammonia and molybdate and do not contain nitrate, and are definite compounds in most cases.

7. The ratio MoO_3 : NH_3 in the precipitate increases as the ratio HNO_3 : MoO_3 in the solution increases.

8. The ratio MoO_3 : NH_3 in the precipitate is decreased by the presence of ammonium nitrate in the solution.

9. Compounds corresponding to the following formulae have been obtained:

1. $(NH_4O)_8MoO(OMoO_2)_7OMoO(ONH_4)_3.4H_2O$

2. $(NH_4O)_8MoO(OMoO_2)_9OMoO(ONH_4)_3.8H_2O$

3. $(NH_4O)_3MoO(OMoO_2)_9OMoO(OH)_3.8H_2O$ and 11 H_2O

4. $(NH_4O)_8MoO(OMoO_2)_{11}OMoO(OH)_3.12H_2O$

5. $(NH_4O)_2(OH)MoO(OMoO_2)_7OMoO(OH)_3.7H_2O$

6. $(NH_4O)_8MoO(OMoO_2)_{14}OMoO(OH)_3.14H_2O$

7. $(NH_4O)_3MoO(OMoO_2)_{15}OMoO(OH)_3.6H_2O$

10. Compounds corresponding to formulae #3, 5, 6 and 7 have not been mentioned previously in the literature.

11. Tridecamolybdate does not represent the limit of condensation of molybdate chains, nor are acid salts possible only at the limit of condensation, as stated by Posternak.

12. An hypothesis for the mechanism of condensation has been proposed.

BIBLIOGRAPHY

1. Svanberg and Struve.
   Jahresb, 1847, p. 412.
   Cited by Hehner (24), p. 23.

2. Sonnenschein.
   Jahresb. 1851, p. 349.
   Cited by Hehner (24), p. 23.

3. Eggertz, V.
   Bestimmung des Phosphorgehalts in Eisen und Eisenerzen mittelst molybdänsauren Ammoniaks.
   J.prakt. Chem. 79, 496 (1860).

4. Pemberton, Henry, Jr.
   The Determination of Phosphoric Acid by the Titration of the Yellow Precipitate with Standard Alkali.
   J. Am. Chem. Soc. 15, 382-395 (1893).

5. Pemberton, H., Jr.
   On the Determination of Phosphoric Acid.
   J. Am. Chem. Soc. 16, 278-282 (1894).

6. Neumann, Albert
   Alkalimetrische Bestimmung der Phosphorsäure unter Benutzung der Sauregemisch-Veraschung.
   Z. physiol. Chem. 37, 129-135 (1903).

7. Gregersen, J. P.
   Uber die alkalimetrische Phosphorsäurebestimmung nach A. Neumann.
   Z. physiol. Chem. 53, 453-463 (1907).

8. Emmerton.
   Blair, Chemical Analysis of Iron.
   J. B. Lippincott & Co., Philadelphia (1888),p. 85.

9. Jones, Clemens
   Phosphorus in Pig Iron, Steel and Iron Ore.
   Chem. News, 62, 220-222 (1890).

10. Jones, Clemens
    A Rapid Method for the Reduction of Ferric Sulfate in Volumetric Analysis.
    Chem. News 60, 93-96 (1889).

11. Blair, Andrew A. and Whitfield, J. Edward
Ammonium Phosphomolybdate and the Reducing Action of Zinc in the Reductor.
J. Am. Chem. Soc. 17, 747-760 (1895).

12. Miller, Edmund H. and Frank, Henry.
On the Reduction of Molybdenum by Zinc and the Ratio of Bismuth to Molybdenum in Bismuth Ammonium Molybdate.
J. Am. Chem. Soc. 25, 919-928 (1903).

13. Noyes, W. A. and Frohman, E.D.
The Volumetric Determination of Phosphorus in Steel.
J. Am. Chem. Soc. 16, 553-559 (1894).

14. Randall, D. L.
Gooch, Methods in Chemical Analysis.
John Wiley & Sons, New York (1912) p. 425.

15. Hundeshagen, Franz.
Analytische Studien uber die Phosphordodekamolybdansaure, die Bedingungen ihrer Bildung und ihrer Abscheidung als Ammoniusalz.
Z. anal. Chem. 28, 141-172 (1889).

16. Baxter, Gregory Paul and Griffin, Roger Castle.
The Determination of Phosphoric Acid by Means of Ammonium Phosphomolybdate (second paper).
Am. Chem. Jour. 34, 204-217 (1905).

17. Posternak, S.
Variations in the Composition of Ammonium Phosphomolybdate.
Compt. rendu. 170, 930-933 (1920).
C. A. 14, 2306 (1920).

18. Baxter, Gregory Paul
The Determination of Phosphoric Acid by Means of Ammonium Phosphomolybdate.
Am. Chem. Jour. 28, 298-315 (1902).

19. Kilgore, B. W.
On the Estimation of Phosphoric Acid by Titration of the Ammonium Phosphomolybdate Precipitate with Standard Alkali.
J. Am. Chem. Soc. 17, 950-968 (1895).

20. Kleinmann, Hans
Uber die Bestimmung der Phosphorsäure. III
Biochem. Z. 99, 95-105 (1919).

21. Falk, K. George and Sugiura, Kanematsu
The Precipitation of Phosphorus as Ammonium Phosphomolybdate in the Presence of Sulfuric Acid.
J. Am. Chem. Soc. 37, 1507-1515 (1915).

22. Carpenter, F. B.
The Determination of Phosphoric Acid by the Official Volumetric Method.
J. Ind. Eng. Chem. 2, 157-8 (1910).

23. Hibbard, P. L.
A Study of the Pemberton-Kilgore Method for the Determination of Phosphoric Acid.
J. Ind. Eng. Chem. 5, 998-1009 (1913).

24. Hehner, Otto
On the Determination of Phosphoric Acid as Phosphomolybdate.
Analyst. 4, 23-29 (1879).

25. Richards, Marion B. and Godden, William
The Pemberton-Neumann Method for the Estimation of Phosphorus.
Analyst, 49, 565-572 (1924)

26. Klason, Peter
Beitrage zur Kenntniss der Molybdänsäure.
B. 34, 153-158 (1901).

27, Mylius, F.
Zur Kenntniss der Molybdänsäure.
B. 36, 638-640 (1903).

28. Posternak, S.
Hexabasic Polymolybdates.
Compt. rendu. 171, 1213-1215 (1920).

29. Rammelsberg.
B. 1877, p. 1776.
Cited by Hehner (24), p. 24.

30. Wood, E. Fred
A Modification of the Molybdate Method of Estimating Phosphorus in Steel.
Chem. News 52, 279-280 (1885).

31. Gladding, Thomas S.
A Gravimetric Method of Estimating Phosphoric Acid as Ammonium Phosphomolybdate.
J. Am. Chem. Soc. 18, 23-27 (1896).

32. Tamm, Adolf
On the Determination of Phosphorus in Iron and Iron Ores.
Chem. News 49, 208-210 (1884).

33. Meineke, C.
Kritische Untersuchungen über die Bestimmung der Phosphorsäure.
Chem. Zeit. 20, 108-113 (1896)

34. Woy.
Die Bestimmung der Phosphorsäure als Phosphorsäuremolybdansäureanhydrid.
Chem. Zeit. 21, 441-443 (1897).

35. Auld, S. J. M.
The Phosphomolybdate Estimation of Phosphoric Acid in Soils.
Analyst, 37, 130-137 (1912).

36. Stutzer, A.
Determination of Phosphoric Acid as Ammonium Phosphomolybdate.
Landw. Versuchs. Stat. 94, 251-264 (1919).
J. Soc. Chem. Ind. 39, 250A (1920).

37. Dienes, L.
Studien zur Quantitative Bestimmung sehr geringer, Ca,- Mg.-. und P-Mengen in tierschen Substanzen.
Biochem. Z. 95, 139 (1919).

38. Bhattacharyya, Haripada
A Rapid Method for the Determination of Phosphorus in Steel.
J. Soc. Chem. Ind. 32, 738 (1913).

39. Samson, Kurt.
Phosphorsäurebestimmungen in kleinen Substangmengen.
Biochem. Z. 164, 288-294 (1925).

40. Iversen, Poul
Untersuchungen über die titrimetrische Phosphorsäurebestimmung nach Neumann.
Biochem. Z. 104, 14-29 (1920).

41. Heubner, Wolfgang
Über den Rechnungsfaktor bei der Phosphorbestimmung nach Neumann.
Biochem. Z. 64, 393-400(1914)

42. Jodidi, S. L.
On the Factor to be Used for the Calculation of the Phosphoric Acid by Neumann's Method.
J. A. Chem. Soc. 37, 1708-1710 (1895)

43. Werner, A.
New Ideas on Inorganic Chemistry.
Longmans Green Co., London (1911) p. 100.

44. Copaux, H.
The Constitution of Paramolybdates and Paratungstates.
Compt. rendu. 156, 1771-1774 (1913).
C. A. 13, 3459.

Acknowledgments

It is my privilege to express my sincere appreciation of the aid given by Doctor Peters, in the suggestion of the problem, in outlining the experimental procedure, and in the preparation of this paper. May I take this opportunity also to thank all those who have been of assistance, especially the members of the Chemistry Department who have offered many helpful suggestions.

Approved by:

C. C. Peters

F. W. Alderman

C. E. Gordon

Graduate Committee

Date: June 7 1937